A Synopsis of the Ph.D. Thesis entitled,

"Catalytical Studies of Synthesized Metal nanoparticles in organic reactions"

To be submitted

to

Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004

For The Degree of

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

By

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“Catalytical studies of synthesized metal nanoparticles in organic reactions”

The world today is experiencing the benefits of metal nanoparticles in a host of different areas not limited to optics, electronics and medicine. Nanotechnology is the application of science to control matter at the molecular level. At this level the properties are significantly different from that of bulk materials. It is also referred to as the term for designing, characterization, production, and application of structures, devices and systems by controlling shape and size at nanometer scale. In scientific terms “nano” means 10^{-9} meter, where 1nm is equivalent to one thousand of micrometer. Nanomaterials can be nanoscale in one dimension (surface film), two dimensions (strands or fibers) or three dimension (particles). They successfully enhance the immobilization and activity of catalyst as nanocrystalline metal oxide. Nanocrystalline material posses high surface to volume ratio and co-ordination parts which provide a larger number of active site per unit area compared to their heterogeneous counter parts. Also depending upon the nature of metal they are utilized both for their acid-base and redox properties and hence belongs to the largest family of heterogeneous catalysis in organic transformation.

The properties of nanomaterials depend sensitively on their size and shape. Therefore, the challenges in nanocrystal synthesis are to control not only the crystal size but also the shape and morphology. In order to produce the desired nonstructural materials various method have been developed such as molecular beam epitaxy, hydrothermal method, chemical reaction, homogeneous precipitation, deposition on support is thin film technology. Of all the methodologies developed for the production of metal nanoparticles, the electrochemical reduction method offers an alternative simple means in organic solvent systems.

Catalysis is a process in which the chemical reaction is facilitated by the presence of catalyst and plays a vital role in nature and society. Literature survey revealed that the organic reactions are carried out using inorganic acid catalysts such as H_2SO_4, HCl, HNO_3

and sometimes Lewis acids. Despite of their high selectivity, these homogeneous classical acid catalysts suffer from several disadvantages, such as high toxicity, corrosive nature, difficult to recover and reuse. Considering these disadvantages in recent years, industry favors catalytical process induced by heterogeneous catalysts over homogeneous process in view of the ease of handling, simple work-up. The main advantage of heterogeneous catalyst is that being a solid material is easy to separate from the reactants and products after the catalytic reaction and is reusable. Surface of metal oxides exhibit acid/base characters and constitute the largest family of heterogeneous catalysts. Many metal oxides especially Al_2O_3, MgO, ZnO and TiO_2, NiO etc. are excellent adsorbents for a wide variety of organic compounds and increase the reactivity of the reactants.

Considering the importance of heterogeneous catalysis, in the present work three new heterogeneous catalysis have been prepared (TiO_2, Ni) mono and bimetallic nanoclusture by using electrochemical method. Our synthetic approach is to control the growth and particle size by introducing 'size control' surfactant and ligands in to the electrochemical system supporting electrolyte and the stabilizer for the resulted nanoparticles; other parameter for controlling the size of nano particles is current density. Pure and size selective nanoparticles were prepared by this method. These were characterized by UV-Visible microscopy, Fourier-Transform Infra Red spectroscopy (FT-IR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectrophotometer (EDS), Transmission electron microscopy (TEM). From these characterizations size, phase/geometry, bonding (stretching and bending modes of vibrations), surface morphology and composition of synthesized nanoparticles were studied.

After having thorough knowledge of physical/ chemical properties and understanding their suitability it was thought to explore catalytic applications of these synthesized material for various organic transformations and these particles were also tested for their antimicrobial activity. As a result of this study, it is observed that these synthesized materials show excellent catalytic and antimicrobial activity.

PRESENT WORK

The work undertaken entitled **"Catalytical studies of synthesized metal nanoparticles in organic reactions"** is presented in the thesis in five chapters. A chapter wise summary of the thesis is given below.

CHAPTER –I

This chapter describes the general introduction and literature survey of nanostructure materials, nano metal oxide, mesoporous materials along with their process of synthesis as have been developed over the years. A comparison of the physicochemical properties of nanomaterials with the bulk materials has been described. It also describes the various methods which are known in the preparation of nanoparticles.

CHAPTER –II

It describes the experimental set up of the electrochemical process for the synthesis of Ti, Ni monometallic and TiNi bimetallic nanoparticles. For the synthesis we have used commercially available pure Ti, Ni metal sheet (1x1 cm) as anode and a platinum sheet (1x1 cm) as the cathode. The two electrodes were parallel and 1 cm apart from each other. Capping agent Tetra Alkyl Ammonium Bromide in acetonitrile: tetrahydrofuran (4:1) served as the supporting electrolyte. Electrolysis was carried out in nitrogen atmosphere. The electrolysis was carried out for 2 hours at room temperature. This chapter is divided into three sections.

Section-I:

This section gives the detail of synthesis of Titanium nanoparticles by electrochemical reduction method. The ligand effect on the particles size was studied using two different ligands namely TPAB and TBAB. The variation in the particles size with respect to current density also studied at $10mA/cm^2$ and $14mA/cm^2$. The Ti nanoparticles thus obtained were characterized by UV-Visible Spectroscopy, Fourier Transform Infra Red Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectrophotometer and Transmission Electron Microscopy.

Section-II:

This section gives the details of synthesis of Nickel nanoparticles by electrochemical reduction method. The ligand effect on the particles size was studied using two different ligands namely TPAB and TBAB. The variation in the particles size with respect to current density also studied at 8mA/cm^2 and 12mA/cm^2. The Ni nanoparticles thus obtained were characterized by UV-Visible Spectroscopy, Fourier Transform Infra Red Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectrophotometer and Transmission Electron Microscopy.

Section-III:

This section describes the synthesis of bimetallic nanoclusters of Ti-Ni with some modification in the experimental set-up. The geometry of the electrodes was arranged in such a way that platinum was at the center and perpendicular were Ti and Ni anodes at either ends. The other conditions were kept constant as in the preparation of monometallic clusters. Only current densities to control the particles were changed to 12 mA/cm^2 and 16mA/cm^2. The characterization was done by UV-Visible Spectroscopy, Fourier Transform Infra Red Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectrophotometer and Transmission Electron Microscopy.

CHAPTER –III

This chapter deals with the antimicrobial studies of synthesized metal nanoparticles against human pathogens like gram negative Escherichia coli (E.coli), S. typhi and gram positive Staphylococcus aureus, B. subtilis strains. This chapter further divided in two sections.

Section-I:

This section describes the experimental procedure for antibacterial and antifungal activities of TiO_2 and Ni monometallic nano clusters. The inhibitory zone and data are presented.

Section-II:

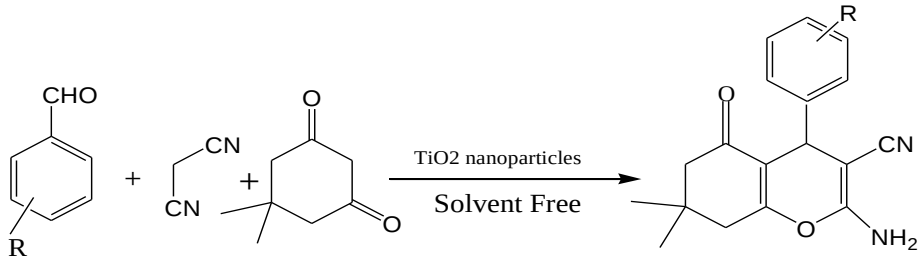
This section includes the experimental procedure for antibacterial and antifungal activities of Ti-Ni bimetallic nano clusters. The results obtained by using bimetallic nano clusters and data are presented.

CHAPTER –IV

In this chapter, catalytic applications of monometallic nanoparticles for various reactions involving synthesis of some biological important compounds are discussed. Moreover, a complete study involving the stability of catalyst in various solvent, screening of catalyst amount and its reusability has been carried out. It is further divided into five sections.

Section-I:

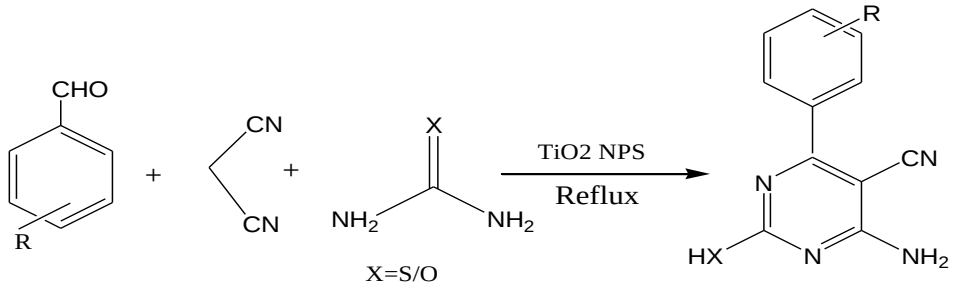
This section includes the synthesis of 4H-benzo[b]pyrans by the cyclocondensation reaction of aldehyde, malononitrile and dimedone by using 50mg of TiO_2 nanoparticles in solvent free condition **(Scheme 1)**. Using this method, all the derivatives have been obtained in good to excellent yield in short reaction time.



(Scheme 1)

Section-II:

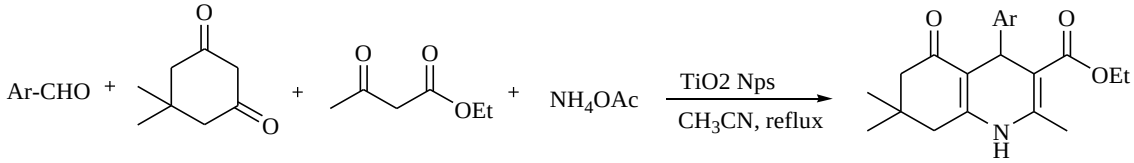
In this section the catalytic activity of Ti nanoparticles has been tested for the Biginelli reaction, by using aromatic aldehyde, malononitrile and urea/thiourea under reflux condition **(Scheme 2)**. The developed protocol has several benefits, such as short reaction time, mild reaction condition, reusability of catalyst.



(Scheme 2)

Section-III:

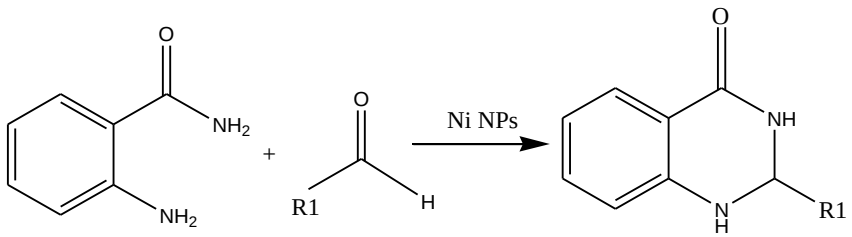
This section includes the one-pot synthesis of polyhydroquinoline derivative by cyclocondentation of aldehyde, dimedione, ethyl acetoacetate and ammonium acetate in presence of TiO_2 nanoparticles in acetonitrile **(Scheme 3)**. This method effort various advantages over the other method used for synthesis of polyhydroquinoline.



(Scheme 3)

Section-IV:

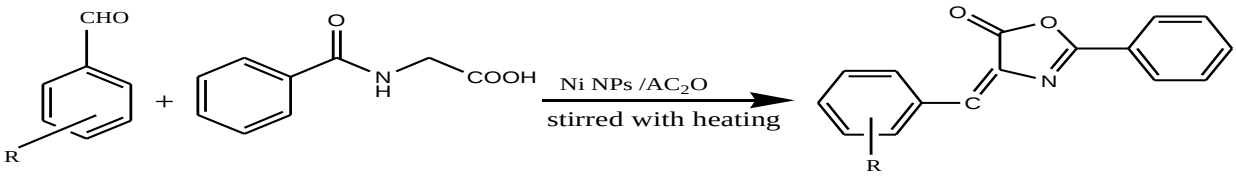
This section deals with the synthesis of 2, 3 dihydro-4(1H)-quinazolinones by reacting aromatic aldehyde with anthranilamide in 10ml methanol as solvent and 50mg Ni nanoparticles as catalyst in ultrasound irradiation **(Scheme 4)**. All the derivatives were synthesized with short reaction time and in excellent yields.



(Scheme 4)

Section-V:

This section reports the use of Ni nanoparticles for the synthesis of 4-aryldiene-2-phenyl-5(4)-oxazolones by reacting aldehyde , hippuric acid , acetic anhydride in 5ml of ethanol with constant stirring and heating **(Scheme 5)**. This method has various advantages such as mild reaction condition, shorter reaction time to get excellent yield of product.



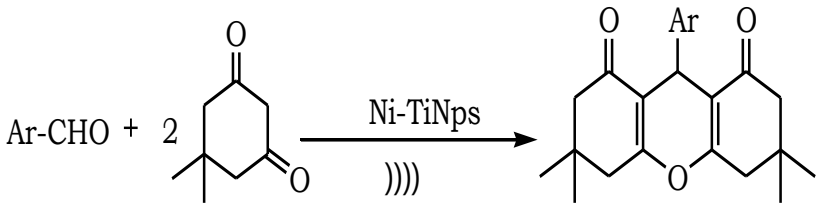
(Scheme5)

CHAPTER –V

This chapter demonstrates the catalytic applications of synthesized bimetallic nanoparticles for the synthesis of various biological or pharmacological important compounds. Furthermore a detailed study involving the stability of catalyst in various solvents, screening of catalyst amount and its recovery and reuse was performed. This chapter further divided into four sections.

Section-I:

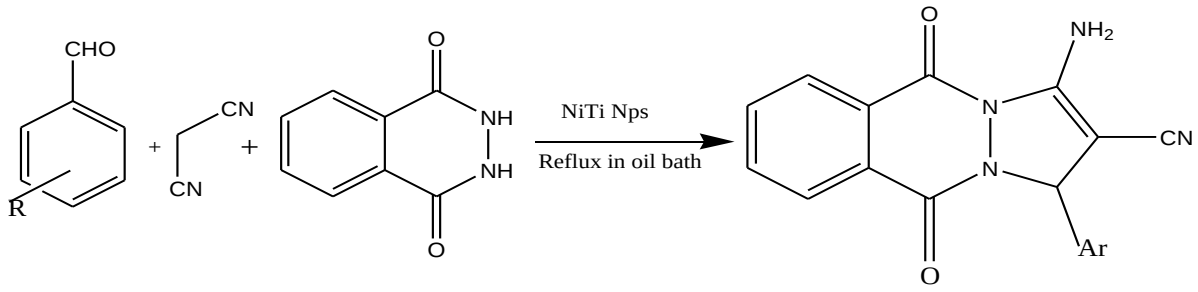
In this section, we reported a mild and high yielding protocol for the synthesis of 1, 8-dioxo-octahydroxanthenes *via* cyclo-condensation of various aldehydes and 1, 3-cyclohexenedione by using Ni Nps as a catalyst **(Scheme1)**.



(Scheme1)

Section-II:

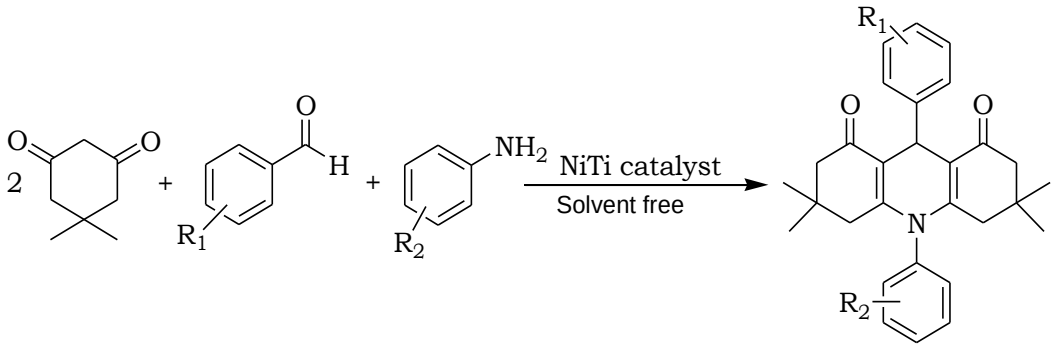
This section describes the efficient, time consuming, high yielding method for the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones via a cyclocondensation reaction of malonitrile, phthalhydrazide, and aromatic aldehydes in presence of Ti-Ni bimetallic nano clusters **(Scheme 2)**.



(Scheme 2)

Section- III:

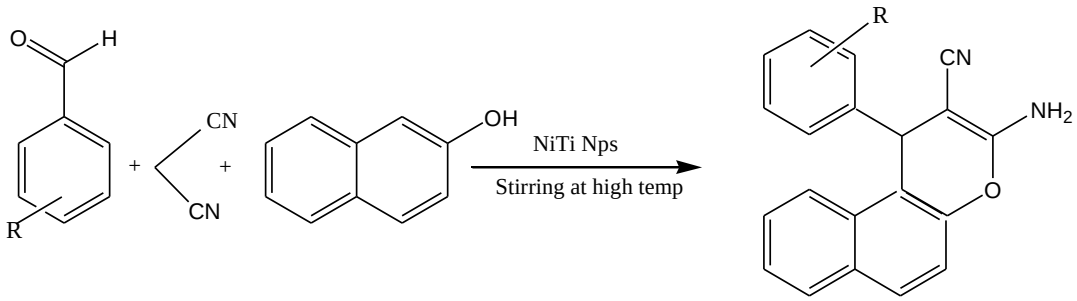
This section provides a new methodology for the preparation of 1, 8 dioxo-decahydroacridine and its derivatives from dimedone, benzaldehyde and aniline in the presence of Ni-Ti in solvent free system **(scheme 3)**. The catalyst was recovered and reused without any noticeable loss of reactivity.



(scheme 3)

Section-IV:

This section describes the efficient, time consuming, high yielding method for the synthesis of 2-amino-4H-Chromenes via a cyclocondensation reaction of malonitrile, β-naphthol and aromatic aldehydes in presence of NiTi bimetallic nano clusters**(Scheme 4)**.



(Scheme 4)

Original Work

Mono and bimetallic nano clusters of Ti, Ni and Ti-Ni have been synthesized by electrochemical reduction method which is used for the first time. The Ti, Ni were used as a sacrificial anode while platinum was used as an inert cathode. The reduction was carried out using a non aqueous solvent. The capping agents used were tetra alkyl ammonium salts which also act as a supporting electrolyte. The nanoclusters have been characterized by different analytical techniques like UV-Visible spectroscopy, Fourier-Transform Infra Red spectroscopy, X-ray diffraction, Scanning electron microscopy, Energy dispersive spectrophotometer, Transmission electron microscopy. The catalytic application of these nanoparticles synthesized by electrochemical reduction method for various organic transformations and their antimicrobial activity was studied for the first time.

Research Student — Research Guide

(Anandgaonker P.L.) — Dr.Anjali S. Rajbhoj